



Synthesis and physical properties of estolides from lesquerella and castor fatty acid esters[☆]

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Abstract

Biodegradable, vegetable oil-based lubricants must have better low temperature properties as well as comparable cost to petroleum oils before they can become widely acceptable in the marketplace. The low temperature property usually measured is the pour point (pp), the minimum temperature at which the material will still pour. Viscosity and viscosity index also provide information about a fluid's properties where a high viscosity index denotes that a fluid has little viscosity change over a wide temperature range. Lesquerella oil is a good candidate for its development into a biodegradable lubricant as it is being developed as an alternative crop for the southwestern U.S. The hydroxy site on the fatty acid (FA) makes it a suitable site for esterification to yield estolides. Castor and lesquerella FA esters were combined with different types of saturated, unsaturated, and branched FAs to produce estolides. Castor and lesquerella estolide esters had the best cold temperature properties when capped with oleic (pp = −54 °C for castor and pp = −48 °C for lesquerella) or capped with a branched material, 2-ethylhexanoic acid (pp = −51 °C for castor and pp = −54 °C for lesquerella). As the saturation was increased in the estolide, pour and cloud points also increased. The increased saturation such as in stearic capped estolides allowed for sufficient alkyl stacking of these long saturated chains producing higher pour points. Oxidative stability of the estolides was compared between the oleic-castor estolide 2-ethylhexyl ester and the coco-castor estolide 2-ethylhexyl ester by the rotating bomb oxidation test (RBOT). The RBOT times for both estolides were low with a similar time of about 15 min. However, when the antioxidant package (3.5 wt.%) was added, the RBOT times increased to 403 min for the coco-castor estolide 2-ethylhexyl ester while still retaining its outstanding cold temperature properties, (pp = −36 °C and cp = −30 °C). The viscosity index ranged from 164 to 200 for these new hydroxy FA derived estolide 2-ethylhexyl esters. These oleic-castor and lesquerella estolide esters have displayed far superior low temperature properties (pp = −54 °C) than any other estolides reported to date. Due to the lack of solvent and catalysts, the cost of these estolides should be reasonable and more suitable as a base stock for biodegradable lubricants and functional fluids than current commercial materials. © 2005 Elsevier B.V. All rights reserved.

Keywords: Castor; Cloud point; Estolides; Lesquerella; RBOT; Pour point

[☆] Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the products, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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1. Introduction

Lesquerella fendleri is a winter annual seed oil crop native to the desert southwestern United States and is currently undergoing an intensive research effort for its successful introduction into agriculture. *Lesquerella* produces a small seed that contains about 30% oil that is comprised of 55–64% hydroxy FA (Carlson et al., 1990a,b). The hydroxy FAs of *lesquerella* (Table 1) (Carlson et al., 1990b) are lesquerolic (55–60%, 14-hydroxy-*cis*-11-eicosenoic acid) and auricolic (2–4%, 14-hydroxy-*cis*-17-eicosenoic acid), a homologue of ricinoleic acid obtained from castor oil. *Lesquerella* production in the past 2 years has averaged 16.2 ha grown each year. In addition, seed yield of 2016 kg ha⁻¹ compared with past releases of 1344 kg ha⁻¹ (Brahim et al., 1996) will jointly allow *lesquerella* to be competitive in the hydroxy oil market.

Unlike normal estolides that are formed when the carboxylic acid functionality of one fatty acid links to the site of unsaturation of another fatty acid to form oligomeric esters, the FA esters of *lesquerella* and castor have a hydroxy functionality that provides a site for esterification to take place to produce estolides. Hydroxy fatty acids such as *lesquerella* can be readily converted into estolides (Penoyer et al., 1954; Hayes and Kleiman, 1995) either as triglycerides in the presence of free fatty acid or from homopolymerization of the split fatty acids. The synthesis of some estolides from castor oil and FA have been reported (Zoleski and Gaetani, 1984; Nelson et al., 2002), but

not as a complete set with the physical properties. *Lesquerella* and castor estolides from the oil were recently reported in a detailed study on the synthesis of triglyceride estolides (Isbell and Cermak, 2002). Hayes and Kleiman (1995) synthesized estolides from the free lesquerolic and oleic acids using a lipase catalyst. However, no reports are available on estolides capped with different FAs or their physical properties.

Numerous publications on biodegradable, renewable functional fluids have appeared over the past several years. Many groups have tried to use the inexpensive commodity prices of soybeans to introduce this traditional U.S. oil source into a functional fluid market (Tilton, 2002). Many reasons exist for this recent movement, a major one being that vegetable oil-based lubricants and derivatives have excellent lubricity and biodegradability properties for which they are being examined as a base stock for lubricants and functional fluids (Mang, 1994, 1997; Legrand and Durr, 1998; Canter, 2001). Two major problems are encountered with vegetable oils as functional fluids: (1) low resistance to thermal oxidative stability (Becker and Knorr, 1996), and (2) poor low temperature performance (Asadauskas and Erhan, 1999; Zehler, 2001). However, with the addition of additive packages, these properties sometimes can be improved, but only at the expense of biodegradability, toxicity, and cost.

Estolides have been shown to have certain physical characteristics that could help eliminate common problems associated with vegetable oils as functional fluids (Cermak and Isbell, 2002). One of the concerns with vegetable oils is their stability toward oxidation. Simple oleic estolides (oligomers of oleic acid), when formulated with a small amount of oxidative stability package, show better oxidative stability than both petroleum and vegetable oil-based fluids (Cermak and Isbell, 2001), but improvements still can be made. Cermak and Isbell (2002) also reported that coco-oleic estolide (coconut oil fatty acids and oleic oligomers) had excellent low temperature properties because the random short chains disrupt the stacking interactions and produce pour points that are considerably lower.

Previous estolide esters have compared favorably with commercially available industrial products such as petroleum-based hydraulic fluids, soy-based fluids, and petroleum oils. In this paper we report the effective synthesis of castor and *lesquerella* 2-ethylhexyl estolide esters along with their physical properties,

Table 1

Chemical composition of *lesquerella* and castor oils^a

FAME	<i>Lesquerella</i> oil (mass%)	Castor oil (mass%)
16:0	1.1	1.0
16:1	0.7	–
18:0	1.8	–
18:1	15.4	3.7
18:2	6.9	4.4
18:3	12.2	–
20:0	0.2	–
20:1	1.0	–
20:2	0.2	–
18:1 Hydroxy	0.6	89.0
20:1 Hydroxy	55.4	1.1
20:2 Hydroxy	3.8	–

^a Determined by GC (SP-2380, 30 m × 0.25 mm i.d.).

such as pour and cloud points, viscosity, and color. Additionally we explored the effects that the placement of the unsaturation has on the physical properties. The biodegradability, lubricating properties (low temperature properties and oxidative stability) and the synthesis of these estolides from lesquerella and castor were compared with commercially available materials.

2. Materials and methods

2.1. Materials

Lesquerella oil was obtained from cold-pressed *Lesquerella fendleri* seed, which was then subsequently alkali refined, bleached, and deodorized. Oleic acid (90%), 2-ethylhexanoic acid, palladium 0.25 wt.% on activated carbon, silica gel (230–400 mesh, 60 Å), and boron trifluoride dimethyl etherate were obtained from Aldrich Chemical Co. (Milwaukee, WI). Castor oil, ethyl acetate and hexane (for extractions), 2-ethylhexanol were obtained from Fisher Scientific Co. (Fairlawn, NJ). Stearic acid was obtained from Pfaltz & Bauer Inc. (Waterbury, CT). Ethanol was obtained from AAPER Alcohol and Chemical Company (Shelbyville, KY). The fatty acid methyl ester (FAME) standard mixtures were obtained from Alltech Associates, Inc. (Deerfield, IL). Solvents for extraction were HPLC grade or an equivalent, and were used without further purification. Petroleum oil: Mobil® 10W-30 and synthetic oil: Castrol Synthetic® 10W-30 was obtained from Wal-Mart Department Store® (Peoria, IL). Soy based oil: Biosoy® was obtained as a free research sample from University of Northern Iowa (Cedar Falls, IA). Hydraulic fluid: Traveller Universal Hydraulic Fluid® was obtained from Tractor Supply Company® (Peoria, IL). Aeroshell® 15W-50 Aviation oil was obtained as a free research sample from the Central Illinois Aviators (Galesburg, IL). Lubrizol 7652 antioxidant package was obtained as a free research sample from The Lubrizol Corporation® (Wickliffe, OH).

2.2. Methods

2.2.1. Gas chromatography (GC)

Gas chromatography analysis was performed with a Hewlett-Packard 6890N Series gas chromatograph (Palo Alto, CA) equipped with a flame-ionization

detector and an autosampler/injector. Analyses were conducted on a SP-2380 30 m × 0.25 mm i.d. column (Supelco, Bellefonte, PA). Saturated C₈–C₃₀ FAMES provided standards for making fatty acid and by-product assignments.

Parameters for SP-2380 analysis were: column flow 1.4 ml/min with helium head pressure of 136 kPa; split ratio 50:1; programmed ramp 120–135 °C at 10 °C/min, 135–175 °C at 3 °C/min, 175–265 °C at 10 °C/min, hold 5 min at 265 °C; injector and detector temperatures set at 250 °C. Retention times for eluted peaks were: methyl stearate 12.33 min, methyl oleate 13.33 min, hydroxy methyl stearate 22.08, hydroxy methyl oleate 22.31, 14-hydroxy eicosanate 23.30, 14-hydroxy-*cis*-11-eicosenate 23.52, 14-hydroxy eicosanate 23.80 min, and 14-hydroxy-*cis*-17-eicosenate 24.00 min.

2.2.2. Rotating bomb oxidation test (RBOT)

Rotating bomb oxidation determinations were conducted on a rotating bomb oxidation test (RBOT) apparatus manufactured by Koehler (Bohemia, NY) using the ASTM method D 2272-98 (ASTM, 1998b). Estolides, free research samples, and commercial products were run at 150 °C. Samples were measured to 50.0 ± 0.5 g with 5.0 ml of water added to the sample. The copper catalyst was measured to 3 m and sanded with 220 grit silicone carbide sand paper produced by Abrasive Leaders and Innovators (Fairborn, OH) and was used immediately. The wire was wound to give an outer diameter of 44–48 mm, a weight of 55.6 ± 0.3 g, and a height of 40–42 mm. The bomb was assembled and slowly purged twice with oxygen. The bomb was charged with 620 kPa of oxygen then tested for leaks by immersing in water. The test was complete after the pressure dropped more than 175 kPa below the maximum pressure. All samples were run in duplicate and the average times were reported. Samples were run neat and with 1.5, 2.5, and 3.5 wt.% of a Lubrizol 7652 antioxidant package dissolved in the oil prior to the test.

2.2.3. Gardner color

Gardner color was measured on a Lovibond 3-Field Comparator from Tintometer Ltd. (Salisbury, England) using AOCS method Td 1a-64 (Firestone, 1994b). Gardner color of both the residue and distillate materials was measured throughout the distillation. The “+”

and “–” notation was employed to designate samples that did not match one particular color.

2.2.4. Viscosity

Viscosity was determined using calibrated Cannon-Fenske viscometer tubes obtained from Cannon Instrument Co. (State College, PA). Measurements were run in a Temp-Trol (Precision Scientific, Chicago, IL) viscometer bath set at 40.0 and 100.0 °C. Viscosity and viscosity index were calculated using ASTM methods D 445-97 (ASTM, 1997) and ASTM D 2270-93 (ASTM, 1998a), respectively. Duplicate measurements were made and the average values were reported.

2.2.5. Pour point (pp)

Pour points were measured by ASTM method D97-96a (ASTM, 1996) to an accuracy of ± 3 °C. The pour points were determined by placing a test jar with 50 ml of the sample into a cylinder submerged in a cooling medium. The sample temperature was measured in 3 °C increments at the top of the sample until the material stopped pouring. This point is determined when the material in the test jar did not flow when held in a horizontal position for 5 s. The temperature of the cooling medium was chosen based on the expected pour point of the material. Samples with pour points that ranged from (+9 to –6, –6 to –24, and –24 to –42 °C) were placed in baths of temperature (–18, –33, and –51 °C), respectively. The pour point was defined as the coldest temperature at which the sample still poured. All pour points were run in duplicate and average values were reported.

2.2.6. Cloud point

Cloud points were determined by ASTM method D 2500-99 (ASTM, 1999) to an accuracy of ± 1 °C. The cloud points were determined by placing a test jar with 50 ml of the sample into a cylinder submerged into a cooling medium. The sample temperature was measured in 1 °C increment at the bottom of the sample until any cloudiness was observed at the bottom of the test jar. The temperature of the cooling medium was chosen based on the expected cloud point of the material. Samples with cloud points that ranged from (room temperature to 10, 9 to –6, and –6 to –24, –24 to –42 °C) were placed in baths of temperature (0, –18, –33, and –51 °C), respectively. The cloud point was defined as the coldest temperature at which the sample

remained opaque. All cloud points were run in duplicate and average values were reported.

2.2.7. Acid value

The acid values were measured on a 751 GPD Titrino from Metrohm Ltd. (Herisau, Switzerland). Acid values were determined by the AOCS Method Te 2a-64 (Firestone, 1994a) with ethanol substituted for methanol to increase the solubility of the estolide ester during the titration. All acid values were run in duplicate and average values were reported.

2.2.8. Hydroxy fatty acid content

Analytical estolide samples for GC were prepared by heating a 10 mg sample of estolide in 0.5 ml of 0.5 M KOH/MeOH to reflux on a heating block for 60 min in a sealed vial. After cooling to room temperature, 2 ml of 1 M H₂SO₄/MeOH were added to the vial. The vial was resealed and heated to reflux on a heating block for 30 min. The solution was transferred into a separatory funnel with water (1 ml) and extracted with hexanes (2 × 2 ml), dried over sodium sulfate, gravity filtered, placed in a GC vial with hexane, sealed, and injected into the GC.

2.2.9. Synthesis

2.2.9.1. Unsaturated fatty acid esters. Acid-catalyzed transesterification reactions were conducted with solvent, 2-ethylhexanol, in a three-neck round bottom flask under vacuum. The flask was evacuated by vacuum (20 Pa) and maintained at 80 °C for 24 h using a heating mantle controlled by a J-Kem Gemini-2 (St. Louis, MO) temperature controller utilizing a temperature probe immersed below the liquid level in the flask. For the synthesis of either lesquerella 2-ethylhexyl esters or castor 2-ethylhexyl esters, a solution of boron trifluoride dimethyl etherate (0.5 M, 126.0 ml) was added to lesquerella oil (1.00 kg, 1.04 mol) and 2-ethylhexanol (1.56 kg, 11.99 mol, 1.84 l). After 24 h, the mixtures were allowed to cool, transferred to a separatory funnel followed by the addition of 200 ml of a 1:1 ethyl acetate:hexane solution. The pH of the organic layer was adjusted to 5.3 to 6.0 with a pH 5 buffer (NaH₂PO₄, 519 g in 4 l H₂O, 3 × 100 ml) followed by saturated NaCl (2 × 50 ml). The organic layer was dried over sodium sulfate and filtered. All reactions were concentrated in vacuo then Kügelrohr-distilled under vacuum (6–13 Pa) at 90 to

Table 2

Physical properties of starting castor and lesquerella materials

Hydroxy FA ester	Pour point (°C)	Cloud point (°C)	Vis@ 40 °C (cSt)	Vis@ 100 °C (cSt)	Viscosity index	Gardner color	Acid value (mg/g)
Castor 2-ethylhexyl ester	−33	<−33	22.0	4.2	93	0	2.06
Saturated castor 2-ethylhexyl ester	9	28	23.1	4.2	66	0	0.67
Lesquerella 2-ethylhexyl ester	−7	−22	15.4	3.7	133	0	5.10
Saturated lesquerella 2-ethylhexyl ester	15	30	13.8	3.6	150	0	1.87

Table 3

Physical properties of unsaturated castor and lesquerella-based estolide

Estolide	Capping FA	Hydroxy FA ester	Product name	Pour point (°C)	Cloud point (°C)	Vis@40 °C (cSt)	Vis@100 °C (cSt)	Viscosity index	Gardner color
A	Oleic	Castor	Oleic-Cas	−54	<−54	34.5	7.6	196	2+
B	Stearic	Castor	Stea-Cas	3	23	41.7	8.6	191	8−
C	Coco ^a	Castor	Coco-Cas	−36	−30	29.0	6.5	186	6−
D	2-Ethylhexanoic	Castor	2-EH-Cas	−51	<−51	70.6	11.8	164	13−
E	Oleic	Lesquerella	Oleic-Les	−48	−35	35.4	7.8	200	3+
F	Stearic	Lesquerella	Stea-Les	3	12	38.6	8.2	195	4−
G	Coco ^a	Lesquerella	Coco-Les	−24	<−24	40.4	8.4	192	17
H	2-Ethylhexanoic	Lesquerella	2-EH-Les	−54	<−54	51.1	10.1	189	8−

^a FAs from coconut oil.

110 °C to remove excess 2-ethylhexanol. The residue then underwent a second Kügelrohr-distillation under vacuum (6–13 Pa) at 180 to 200 °C to yield the purified 2-ethylhexyl esters (Table 2) as a light yellow liquid.

2.2.9.2. Hydrogenation fatty acid esters. Hydrogenation was performed by combining hydroxy FA ester i.e. lesquerella 2-ethylhexyl ester (311.0 g, 710.0 mmol), hexane (200 ml), and 0.25 wt.% Pd (1.24 g) on activated carbon into a stainless steel pressure reactor (Pressure Products Industries, Warminster, PA). The reactor was charged to 1379 kPa hydrogen after first purging with hydrogen. A room temperature setting was maintained and the reactions (Table 2) were stirred for 2 to 5 h until hydrogen consumption ceased. The product was separated from catalyst by vacuum filtration through silica and #50 Whatman filter paper. The saturated fatty ester

was then dried over sodium sulfate and filtered. All products were concentrated in vacuo. A 10 mg sample was converted into its methyl ester and injected onto the GC to confirm saturation of the fatty ester.

2.2.9.3. Saturated and unsaturated estolide esters. For saturated and unsaturated lesquerella and castor estolides, saturated and unsaturated lesquerella and castor esters were combined with the corresponding fatty acid as listed in Tables 3 and 4. In most cases, lesquerella 2-ethylhexyl ester (200.0 g, 456.6 mmol) or castor 2-ethylhexyl ester (200.0 g, 487.8 mmol) 1.0 equivalents and a capping material, i.e., oleic acid (195.9 g, 684.9 mmol) 1.5 equivalent as listed in Table 3 were combined in a three-neck round bottom. The flask was fitted with temperature probe, vacuum adapter and a stopper. The reaction was performed

Table 4

Physical properties of saturated castor and lesquerella-based estolide

Estolide	Capping FA	Hydroxy FA ester	Product name	Pour point (°C)	Cloud point (°C)	Vis@40 °C (cSt)	Vis@100 °C (cSt)	Viscosity index	Gardner color
HA	Oleic	Castor	Oleic-H-Cas	−36	<−36	68.3	12.2	178	16+
HB	Stearic	Castor	Stea-H-Cas	6	r.t.	43.6	8.7	186	7+
HC	Oleic	Lesquerella	Oleic-H-Les	−12	−6	37.0	7.9	196	9+
HD	Stearic	Lesquerella	Stea-H-Les	6	31	45.7	9.1	187	6+

under vacuum; the flask was evacuated by vacuum (20 Pa) and held at 200 °C for 24 h using a heating mantle controlled by a J-Kem Gemini-2 (St Louis, MO) temperature controller utilizing a temperature probe immersed below the liquid level in the flask. When the reaction time was reached, the solution was allowed to cool to room temperature under vacuum. All reactions underwent K ugelrohr-distillation under vacuum (6–13 Pa) at 180–200 °C.

2.2.10. Nuclear magnetic resonance (NMR)

¹H and ¹³C NMR spectra were obtained on a Bruker ARX-400 (Karlsruhe, Germany) with a 5 mm dual proton/carbon probe (400 MHz ¹H/100.61 MHz ¹³C) using CDCl₃ as a solvent in all experiments. The assignments of protons were not to the whole number and reflected the actual NMR numbers.

2.2.10.1. ¹H and ¹³C NMR of oleic-castor estolide 2-ethylhexyl ester A (Table 3). ¹H NMR: δ 5.49–5.37 (m, 3.8 H, –CH=CH–), 4.89–4.83 (m, 1.0 H, –CH–OC=O–), 3.98 (d, J=5.7 Hz, 1.8 H, –OCH₂–CH(CH₂–)CH₂–), 2.32–2.24 (m, 6.0 H, –CH₂(C=O)–O–CH₂–, –CH₂(C=O)–O–CH–), 2.06–1.95 (m, 5.6 H, –CH₂–CH=CH–CH₂–), 1.65–1.19 (m, 51.6 H, –CH₂–), and 0.90–0.85 ppm (m, 11.8 H, –CH₃). ¹³C NMR: δ 173.9 (s, C=O, ester), 173.5 (s, C=O, estolide), 132.4 (d, –CH=CH–), 129.9 (d, –CH=CH–), 126.6 (d, –CH=CH–), 124.2 (d, –CH=CH–), 73.5 (d, –CH–O–C=O), 66.5 (t, –O–CH₂–CH–), 38.6 (d, –CH₂–CH(CH₂–)CH₂–), 34.6 (t), 34.3 (t), 33.5 (t), 31.9 (t), 31.6 (t), 30.3 (t), 29.7 (t), 26.6 (t), 29.4 (t), 29.2 (t), 29.1 (t), 29.0 (t), 28.8 (t), 27.2 (t), 27.1 (t), 25.2 (t), 25.0 (t), 24.9 (t), 23.6 (t), 22.9 (t), 22.5 (t), 14.0 (q, –CH₃), 13.9 (q, –CH₃), 13.9 (q, –CH₃), and 10.9 ppm (q, –CH₃).

2.2.10.2. ¹H NMR and ¹³C of stearic-saturated-castor estolide 2-ethylhexyl ester HB (Table 4). ¹H NMR: δ 4.87–4.81 (m, 1.0 H, –CH–OC=O–), 3.97 (d, J=5.7 Hz, 2.0 H, –OCH₂–CH(CH₂–)CH₂–), 2.30–2.23 (m, 4.6 H, –CH₂(C=O)–O–CH₂–, –CH₂(C=O)–O–CH–), 1.63–1.20 (m, 75.7 H), and 0.91–0.86 ppm (m, 10.7 H, –CH₃). ¹³C NMR: δ 174.0 (s, C=O, ester), 173.6 (s, C=O, estolide), 73.9 (d, –CH–O–C=O), 66.5 (t, –O–CH₂–CH–), 38.6 (d, –CH₂–CH(CH₂–)CH₂–), 34.3 (t), 34.1 (t), 31.8 (t), 31.6 (t), 30.32 (t), 29.6 (t), 29.6 (t), 29.5 (t), 29.4 (t),

29.3 (t), 29.2 (t), 29.2 (t), 29.2 (t), 29.1 (t), 28.8 (t), 25.2 (t), 25.0 (t), 24.9 (t), 23.7 (t), 22.9 (t), 22.6 (t), 22.5 (t), 13.9 (q, –CH₃), 13.9 (q, –CH₃), 13.8 (q, –CH₃), and 10.8 ppm (q, –CH₃).

3. Results and discussion

The FA composition for both the hydroxy oils, lesquerella and castor, which contain primarily hydroxy FAs is listed in Table 1. The hydroxyl functionality served as a site for esterification with different FAs to give a new class of estolides (Fig. 1). Hydroxy triglycerides of lesquerella and castor oil were converted into their corresponding hydroxy fatty acid esters (Table 2). Tables 3 and 4 outline a series of reactions (Fig. 1) that explore the effects on the physical properties as the unsaturation placement in the estolide was varied, i.e., on the base unit or on the capping material.

Previously, estolides were formed by carbocationic homo-oligomerization of unsaturated fatty acids (Isbell et al., 1994) from the addition of a fatty acid carboxyl adding across the olefin. This condensation continues to produce the oligomeric compounds called estolides. For castor and lesquerella fatty acid esters, with a site for esterification already in place, esterification could proceed by condensation of the hydroxyl functionality of the hydroxy FA ester with the carboxylic acid function of another FA, i.e., oleic acid. Consequently, the estolide synthesis is terminated at this point from further growth. Thus, we term the estolide as being “capped” (Cermak and Isbell, 2002) because no additional reaction sites are available to further the esterification process. By driving off water, the major byproduct of the reactions, under vacuum and elevated temperatures, the corresponding estolides were produced with good yields (~90%).

The castor and lesquerella oils were converted to their corresponding hydroxy FA esters in modest yields (>80%). The byproduct of this transesterification was the formation of hydroxyl compounds linking together to form oligomeric castor and lesquerella homo-estolides previously synthesized by Achaya (1971). These homo-estolides and excess 2-ethylhexanol were removed via distillation.

A series of reactions (Fig. 1) that explored the formation of estolides with castor and lesquerella

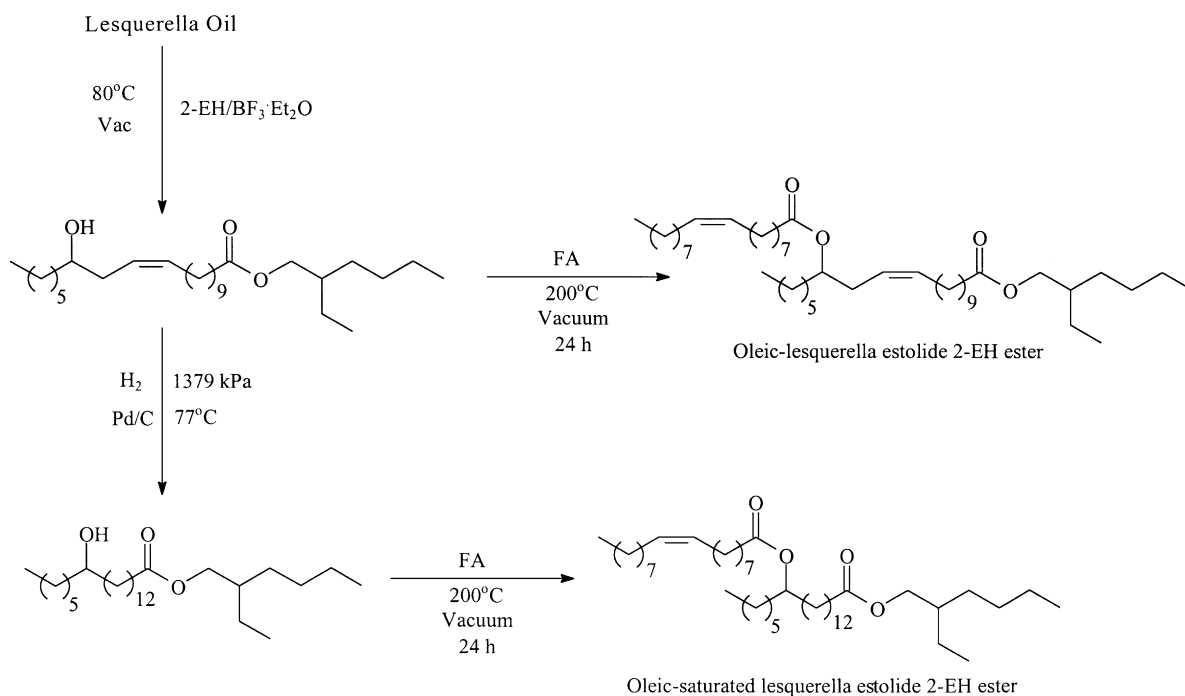


Fig. 1. Reaction scheme for the formation of lesquerella estolides.

and different capping FA are outlined in Table 3. These reactions were done without solvent, under vacuum, and at elevated temperatures. Vacuum distillation removed any excess FA providing the estolide samples. The pour and cloud points, viscosity, viscosity index, and color of these estolides are reported in Table 3.

Saturated hydroxyl-based estolides were also explored to determine the effects of the placement of the unsaturation in the estolides (Fig. 1). Unsaturated hydroxyl FA esters were hydrogenated under standard conditions to yield the saturated FA esters. These esters were then combined with either oleic or stearic FA to produce estolides. Vacuum distillation removed any excess FA to provide the estolide samples. The pour and cloud points, viscosity, viscosity index, and color of these estolides are listed in Table 4.

Isbell and Cermak (2002) reported that a decomposition product was produced at 200 °C in the synthesis of castor and lesquerella triglyceride (TG) estolides. Upon formation of the TG-estolide, deacylation occurred to produce conjugated dienes (Fig. 2). The deacylation was not detected with the formation of estolides from the hydroxy FA esters in this study.

Castor and lesquerella FA esters have pour points of -33 and -27 °C, respectively (Table 2). In the case where the castor and lesquerella base units are unsaturated, the estolides produced that had the lowest pour points were capped with oleic acid ($pp = -54$ °C and $pp = -48$ °C) or with a branched material, 2-ethylhexanoic acid ($pp = -51$ °C and $pp = -54$ °C), respectively (Table 3). By capping the FA esters, the compounds no longer had the opportunity to undergo either intra- or intermolecular hydrogen bond interactions, thus yielding a lower pour point. As the capping material went to a saturated FA, dramatic changes occurred in the physical properties, stearic ($pp = 3$ °C castor and $pp = 3$ °C lesquerella) and coco ($pp = -36$ °C castor and $pp = -24$ °C lesquerella), respectively (Table 3). The stearic group has a higher pour point than the base FA esters because the long saturated alkyl group allows for sufficient alkyl stacking. With shorter branched chains, the opposite was observed with coco and 2-ethylhexanoic (Table 3, D and H). The shorter branched chains disrupt the stacking interactions and produce pour points that are considerably lower than the underivatized FA esters,

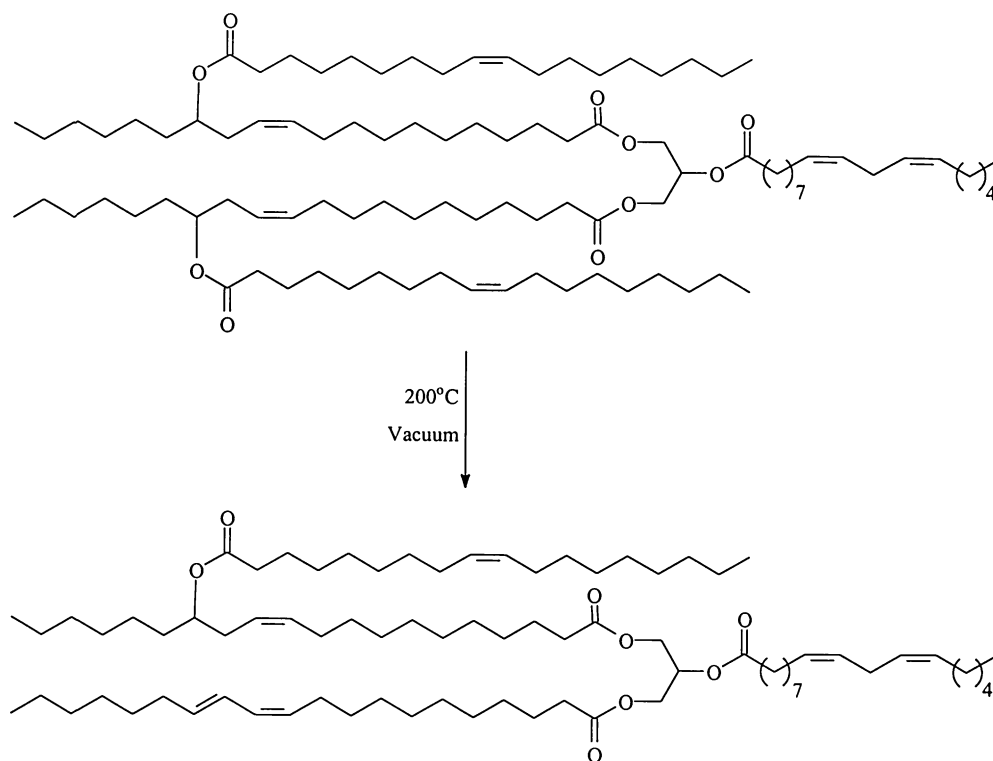


Fig. 2. Reaction scheme for the deacylated triglyceride estolide.

respectively. It has been previously demonstrated that coco capped estolides have beneficial effects on the cold temperature properties of estolides (Cermak and Isbell, 2003b).

As the base of the estolide was changed to a saturated unit, castor and lesquerella castor FA esters had pour points of 9 and 15 °C, respectively (Table 2). These saturated base unit esters were combined with either oleic or stearic acids. The oleic capped estolides had reasonable pour points (pp = −36 °C castor and pp = −12 °C lesquerella) where as the stearic capped material allowed for sufficient alkyl stacking, thus producing higher pour points (Table 4).

Some of the estolides synthesized from castor and lesquerella FA have outstanding pour points (<−50 °C) (Fig. 3). The best estolides to date had been a cuphea-oleic estolide with a pour point of −42 °C (Cermak and Isbell, 2004). The general trend for the best pour point is 2° of unsaturation equals one estolide capped with some branching (2-EH-Les and 2-EH-Cas) followed by an estolide with one degree of unsaturation

either as a capper or on the base unit (pp = −33 °C, coco-cas).

The oxidative stability of vegetable oils is very poor, whereas past estolides increase the oxidative stability by reducing the amount of unsaturation in the molecule

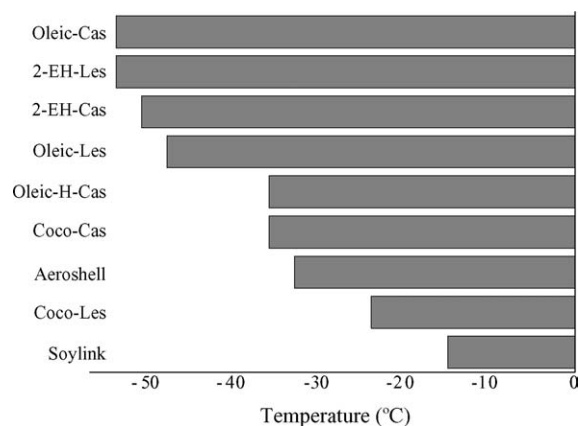


Fig. 3. Estolides pour point comparisons.

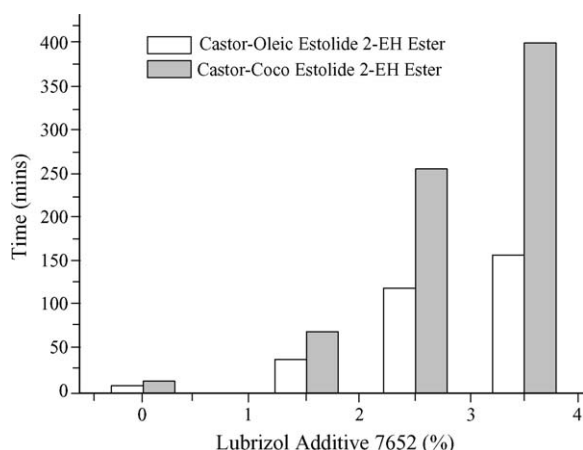


Fig. 4. RBOT time vs. the amount of oxidative stability additive package.

(Cermak and Isbell, 2003a). Estolides synthesized from hydroxy FAs do not decrease the unsaturation in the molecule, and therefore, improvements in the oxidative stability from the formation of estolide are unlikely. This was shown to be the case when pure estolide was tested for oxidative stability; RBOT times were 15 min (Fig. 4). The RBOT times for the estolides tested increased as the amount of antioxidant package was increased (Fig. 4). The unsaturated castor based oleic estolide with only the addition of 3.5% antioxidant stability package compared favorably with commercially available petroleum oils (Table 5). As the “capping” unit was replaced with a saturated version, increased RBOT times were observed (Fig. 4). The coco-castor estolide 2-ethylhexyl ester had RBOT times that exceeded most commercial available materials with the

addition of only 3.5% of the oxidative stability package. Fortunately, the cold temperature properties of these partially hydrogenated materials still exceeded the commercially available materials (Table 5).

The physical properties of various commercial materials were compared with the better performing castor and lesquerella estolide 2-ethylhexyl esters (Table 5). The three estolide 2-ethylhexyl esters selected for comparison with the commercial products were based on their best cold weather performances (Table 3, A and H; Table 4, H and A). These estolide 2-ethylhexyl esters were completely unformulated unlike the commercial products, which contained up to 40% additives designed to improve cold temperature and oxidative stability properties. All the commercial products in Table 5 have cold weather-functional pour points except the soy-based oil. Soy-based products have been demonstrated to have pour points too high for cold weather climates (Erhan and Asadauskas, 2000). All of the commercial products listed had higher cloud points than the castor and lesquerella estolide 2-ethylhexyl esters. A high cloud point could lead to filter plugging and poor pumpability in cold weather applications. The lack of low cloud points in commercially available oils demonstrates the need for a better cold weather performing oil.

The ^1H NMR for the castor and lesquerella estolide esters, specifically estolide ester A (Table 3), shows some key features of a typical estolide. The ester methine signal at 4.85 ppm is indicative of an estolide linkage. Another distinctive feature is the α -methylene hydrogen (2.28 ppm) adjacent to the ester. The carbon NMR spectrum also contains the expected estolide key signals. Distinctive signals are present at 173.5 ppm

Table 5

Comparison of low temperature properties and viscosity index of lesquerella and castor estolide 2-ethylhexyl esters to commercial lubricants

Lubricant	Pour point ($^{\circ}\text{C}$)	Cloud point ($^{\circ}\text{C}$)	Vis@ 40 $^{\circ}\text{C}$ (cSt)	Viscosity index	RBOT (min)
Commercial petroleum oil ^a	−27	2	66.0	152	228
Commercial synthetic oil ^a	−21	−10	60.5	174	256
Commercial soy based oil ^a	−18	1	49.6	220	28
Commercial hydraulic fluid ^a	−33	1	56.6	146	464
Aviation oil ^a	−33	−30	20.4	170	552
Oleic-Cas (Table 3, A) ^b	−54	<−54	34.5	196	159 ^c
Oleic-H-Cas (Table 4, A) ^b	−36	<−36	68.3	178	403 ^c
2-EH-Les (Table 3, H) ^b	−54	<−54	51.1	189	—

^a Commercial, fully formulated material from local vendors.

^b Unformulated.

^c Formulated with 3.5% of an Lubrizol oxidative stability package (7652).

(estolide ester) and the methine carbon at 73.5 ppm, common to estolides. These major peaks in the carbon NMR are also confirmed by a DEPT experiment. The alkene carbons are noticeable in this sample and were completely absent in the saturated version (Table 4, HB).

4. Conclusions

Estolides have been synthesized from a different source of fatty acids with no catalysts and solvent to produce materials that have good cold temperature properties. Estolides synthesized from castor and lesquerella FA esters with oleic acid (pp = -54°C and pp = -48°C) and 2-ethylhexanoic acid (pp = -51°C and pp = -54°C), respectively, yielded the best performing estolides to date. These new estolides from castor and lesquerella FA esters have outperformed commercial products in cold temperature properties even without additives. As the series of estolides were constructed, an evaluation of placement of the double bond relative to the cold temperature properties was performed. Generally, as the saturation in the molecule increased, the pour points increased, whereas the RBOT oxidative stability decreased. The key approach is to maintain some unsaturation to keep low temperature properties while not sacrificing oxidative stability.

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